

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 04-161245

(43)Date of publication of application : 04.06.1992

(51)Int.Cl.

B01J 13/02
C01G 9/02
C09K 3/00

(21)Application number : 02-289719

(71)Applicant : HAYASHI KINZOKU
KOGYOSHO:KK

(22)Date of filing : 26.10.1990

(72)Inventor : INOUE HIROYUKI
TAKIGAMI TOSHIKATSU
HAJIRI NOBUYUKI
MORINAKA YASUSHI

(54) CAPSULATED ZINC WHITE

(57)Abstract:

PURPOSE: To stabilize activity of the surface of zinc white and increase the wetting properties of zinc white to various binders by covering the surface of zinc white with a coat which can be adjusted to be either hydrophilic or hydrophobic.

CONSTITUTION: Zinc white is coated with a cyclohexane inorganic compound having a cyclohexane bond in a main chain or an acrylic organic compound having an acryloyl group or a methacryloyl group in a main chain, alone or in combination. If the surface of zinc white is coated with a film which can be adjusted to be either hydrophilic or hydrophobic, the surface activity of zinc white can be stabilized and also can be applied to hydrophilic and hydrophobic binders. Consequently, the applicable range of zinc white is expanded.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

(19) Japanese Patent Office (JP)

(11) Publication Number

(12) **Laid Open Patent Publication (A)**

9-104834

(43) Laid Open 22 April 1997

(51) Int. Cl. ⁶

C09D 5/00 PPU

C09C 3/10 PBW

C09D 11/02 PTF

17/00 PUJ

167/02 PLD

175/04 PHN

201/06 PDF

Examination Not Yet Requested
Number of Claims 15 (Total 19 pages)

(21) Application Number 8-200313

(22) Filing Date 30 July 1996

(31) Priority Number 7-203238

(32) Priority Date 9 August 1995

(33) Priority Country Japan (JP)

(71) Applicant 000002886

Dainippon Ink & Chemicals, Inc

35-58 Sakashita 3-chome, Itabashi-ku, Tokyo

(72) Inventors T. Hashizume, M. Asada, N. Tashiro, and N. Takao

(74) Representative Patent Agent K. Takahashi

(54) **[Title of the Invention]** Process for producing aqueous pigment dispersion, and aqueous colouring agent composition

(57) **[Abstract]**

[Effect] To provide a process for producing a finely dispersed aqueous pigment dispersion that gives coated material having excellent gloss, colouring properties and colouring power, and also excellent durability and fastness characteristics such as water

resistance; and an aqueous colouring agent composition containing the aqueous pigment dispersion.

[Solution Means] A process for producing an aqueous pigment dispersion, the process comprising a step (1), using a pigment and a resin having a carboxyl group and a cross-linkable functional group or a self cross-linkable functional group, of precipitating the resin so as to make it adhere to the pigment by making the pH of a pigment aqueous dispersion neutral or acidic using an acidic compound, the pigment aqueous dispersion being formed by neutralizing the carboxyl group of the resin with a basic compound so as to make it hydrophilic, a subsequent step (2) of redispersing in an aqueous medium the pigment to which the resin (B) is adhered by neutralizing the carboxyl group of the resin using a basic compound, and cross-linking the resin at any time after the pigment aqueous dispersion is obtained; and an aqueous colouring agent composition containing the aqueous pigment dispersion.

[Claims]

[Claim 1] A process for producing an aqueous pigment dispersion, the process comprising:

a step (1), using a pigment (A) and a resin (B) having a carboxyl group and a cross-linkable functional group, of precipitating the resin (B) so as to make it adhere to the pigment (A) by making the pH of a pigment aqueous dispersion (1a) neutral or acidic using an acidic compound (E), the pigment aqueous dispersion (1a) being formed by neutralizing the carboxyl group of the resin (B) with a basic compound (F1) so as to make it hydrophilic;

a subsequent step (2) of redispersing in an aqueous medium the pigment to which the resin (B) is adhered by neutralizing the carboxyl group of the resin (B) using a basic compound (F2); and

adding a cross-linking agent (C) at any time,

wherein the cross-linkable functional group of the resin (B) and the cross-linking agent (C) are cross-linked at any time after the pigment aqueous dispersion (1a) is obtained.

[Claim 2] The production process according to Claim 1 wherein as the pigment aqueous dispersion (1a) there is used a pigment aqueous dispersion obtained by kneading the pigment (A) and the resin (B) in an organic solvent medium, adding the cross-linking agent (C) before or after the kneading, at least partly neutralizing the carboxyl group of the resin (B) using the basic compound (F1) before and/or after the kneading, and dispersing in an aqueous medium.

[Claim 3] The production process according to Claim 1 wherein as the pigment aqueous dispersion (1a) there used is a pigment aqueous dispersion obtained by mixing and/or kneading the pigment (A), the resin (B) whose carboxyl group has been neutralized using the basic compound (F1), and the cross-linking agent (C) in an aqueous medium.

[Claim 4] The production process according to any one of Claims 1, 2, or 3 wherein the resin (B) is a vinyl-based copolymer, a polyester resin, or a polyurethane resin.

[Claim 5] The production process according to any one of Claims 1, 2, 3, or 4 wherein the acid value based on the carboxyl group of the resin (B) is in the range of 30 to 120 mg KOH/g of resin solids content.

[Claim 6] The production process according to any one of Claims 1, 2, 3, 4, or 5 wherein the cross-linkable functional group of the resin (B) is a carboxyl group and the cross-linking agent (C) is a cross-linking agent selected from the group consisting of an amino resin and a compound having at least two epoxy groups in one molecule, or the cross-linkable functional group of the resin (B) is a hydroxyl group and the cross-linking agent (C) is an amino resin.

[Claim 7] The production process according to any one of Claims 1 to 6 wherein the cross-linkable functional group of the resin (B) and the cross-linking agent (C) are cross-linked before the acidic compound (E) is added or after the pigment (A) to which the resin (B) is adhered is redispersed in the aqueous medium.

[Claim 8] A process for producing an aqueous pigment dispersion, the process comprising:

a step (1), using a pigment (A) and a resin (D) having a carboxyl group and a self cross-linkable functional group, of precipitating the resin (D) so as to make it adhere to the pigment (A) by making the pH of a pigment aqueous dispersion (1b)

neutral or acidic using an acidic compound (E), the pigment aqueous dispersion (1b) being formed by neutralizing the carboxyl group of the resin (D) with a basic compound (F1) so as to make it hydrophilic; and

a subsequent step (2) of redispersing in an aqueous medium the pigment (A) to which the resin (D) is adhered by neutralizing the carboxyl group of the resin (D) using a basic compound (F2);

wherein the resin (D) is self cross-linked at any time after the pigment aqueous dispersion (1b) is obtained.

[Claim 9] The production process according to Claim 8 wherein as the pigment aqueous dispersion (1b) there is used a pigment aqueous dispersion (1b) obtained by kneading the pigment (A) and the resin (D) in an organic solvent medium and at least partly neutralizing the carboxyl group of the resin (D) using the basic compound (F1) before the kneading and/or after the kneading, and dispersing in an aqueous medium.

[Claim 10] The production process according to Claim 8 wherein the pigment aqueous dispersion (1b) used is obtained by mixing and/or kneading in an aqueous medium the pigment (A) and the resin (D) whose carboxyl group has been neutralized using the basic compound (F1).

[Claim 11] The production process according to any one of Claims 8, 9, or 10 wherein the resin (D) is a vinyl-based copolymer, a polyester resin, or a polyurethane resin.

[Claim 12] The production process according to any one of Claims 8, 9, 10, or 11 wherein the acid value based on the carboxyl group of the resin (D) is in the range of 30 to 120 mg KOH/g of resin solids content.

[Claim 13] The production process according to any one of Claims 8, 9, 10, 11 or 12 wherein the self cross-linkable functional group of the resin (D) is (1) one with a carboxyl group and an epoxy group in one molecule, (2) one with a hydroxyl group and an N-alkoxymethylamide group in one molecule, or (3) a radically polymerisable unsaturated group.

[Claim 14] The production process according to any one of Claims 8 to 13 wherein the resin (D) is self cross-linked before the acidic compound (E) is added or after the pigment (A) to which the resin (D) is adhered is redispersed in the aqueous medium.

[Claim 15] An aqueous colouring agent composition characterized in that it comprises an aqueous pigment dispersion produced by the production process according to any one of Claims 1 to 14.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

The present invention relates to a process for producing an aqueous pigment dispersion that is useful for an aqueous colouring agent composition such as a water-based paint, a water-based ink, a printing agent, a colour filter, a jet ink, or a colour toner.

[0002]

[The Prior Art]

From the viewpoint of pollution prevention and occupational health, there is a strong trend towards aqueous based materials in industries using colouring agents such as paints and inks.

[0003]

In order to disperse in an aqueous medium a pigment used for an aqueous colouring agent, a method in which powdered pigment is dispersed using a surfactant or a water-soluble resin is generally employed and is currently widely carried out. However, a paint containing a pigment dispersed using a surfactant has the problem that the coating so obtained has extremely poor water resistance and its applications are limited. Dispersing a pigment in an aqueous medium containing a water-soluble resin is generally more difficult than dispersing a pigment in an organic solvent medium, and it is difficult to disperse the pigment finely at a high level and maintain it stably in that state.

[0004]

On the other hand, in the case where a pigment is simply dispersed using a water-soluble resin, the bond between the pigment and the resin is only due to adsorption, which is weak bonding, and even if it is finely dispersed immediately after it

is produced, since the pigment aggregates over time there is the problem that the storage stability is not good.

[0005]

As a method for obtaining an easily dispersible pigment, the so-called acid precipitation method is known, in which an acid is added to a pigment aqueous dispersion, which is formed by dispersing the pigment in a resin having a carboxyl group neutralized with a base, so as to make the resin hydrophobic, thus making the resin adhere to the pigment.

[0006]

For example, a technique for obtaining a well-dispersed powdered pigment by making rosin adhere to the pigment by the acid precipitation method is known. Since rosin has a small molecular weight, it cannot be a coating-forming resin, and since its weather resistance is poor, the amount of rosin used cannot be increased, and in the current situation the amount thereof used should be limited to on the order of 10 wt % or less. Because of this, if rosin, which is currently used as a pigment treatment agent for a powdered pigment, is used in an aqueous pigment dispersion as in the present invention, the use of rosin alone cannot give a stable aqueous pigment dispersion, and there is the problem that the coating so obtained has poor performance.

[0007]

In order to solve this problem, JP-A-50-122528 and JP-B-61-11979 disclose methods for obtaining a powdered or a solid pigment by carrying out acid precipitation using a specified resin, which is an acrylic resin having a comparatively high molecular weight.

[0008]

However, in either of these methods, since powdering or solidifying is carried out after acid precipitation, pigment particles aggregate considerably during these processes, and when used in a water-based paint or a water-based ink there is the problem that it is necessary to carry out a kneading step again, which takes time and effort. Moreover, although the powdered or solid pigments obtained by these methods can be dispersed easily compared with an untreated powdered pigment there is the problem that it requires considerable effort to finely disperse the once-powdered or

solidified pigment to a degree such that an aqueous colouring agent can exhibit high colouring properties and high colouring power.

[0009]

US Pat. No. 4,166,811 discloses a method for obtaining a pigment that can be dispersed easily in an aqueous medium by re-neutralizing a highly hydrophilic water-soluble resin with a basic compound after acid precipitation.

[0010]

The basic constitution of this method is a method of powdering or solidifying after re-neutralizing with the basic compound, and it is stated that redispersion in an aqueous medium can be carried out only by simple stirring. However, the problem of once-powdered or solidified pigment re-aggregating cannot be ignored, and in order for a high level of colouring properties and colouring power to be exhibited in coated material, simple stirring is not sufficient. Furthermore, in order to make redispersion in an aqueous medium easy after powdering or solidifying, resins that can be used in this method should have a low molecular weight and quite a high acid value, and a coating formed using this as a colouring agent has extremely low toughness and water resistance.

[0011]

[Problems to be Solved by the Invention]

With regard to a coating-forming resin used in an aqueous coating agent, since physical properties such as toughness and durability characteristics such as water resistance of the resulting coating are important, it is necessary for the coating-forming resin to have a molecular weight of a certain degree or higher. In order for the water resistance of the resulting coating not to be lowered, it is often designed so that the proportions of hydrophilic groups such as carboxyl groups and various functional groups effective in dispersing a pigment are low. Using an aqueous coating-forming resin that has been designed at this kind of level, it is therefore extremely difficult to finely disperse the pigment at a high level.

[0012]

That is, an aqueous pigment dispersion that can simultaneously achieve a fine dispersion of the pigment and a high level of durability characteristics such as water

resistance of coated material cannot be obtained in accordance with the conventional techniques.

[0013]

An object of the present invention is to provide a process for producing an aqueous pigment dispersion that can be finely dispersed, has good storage stability, and can form a coating that has excellent water resistance, durability and fastness, which cannot be achieved by the above-mentioned conventional techniques.

[0014]

[Means for Solution of the Invention]

As a result of an intensive investigation by the present inventors in order to solve the above-mentioned problems, it has been found that an aqueous pigment dispersion that is finely dispersed to a degree such that a high level of gloss, colouring properties, and colouring power can be exhibited, has excellent storage stability, has no problem of solvent shock and colour separation, and can give coated material having excellent water resistance, durability and fastness can be produced by a process comprising making the pH of a pigment aqueous dispersion, which has been finely dispersed with a cross-linkable resin having a carboxyl group that has been neutralized with a basic compound, neutral or acidic with an acidic compound to make the resin hydrophobic so as to make the resin adhere strongly to the pigment (hereinafter, this step is also called 'acid precipitation'), and subsequently redispersing in water by neutralizing the carboxyl group once again with a basic compound, wherein the resin is cross-linked at any stage after the pigment aqueous dispersion is obtained, for example, before the acid precipitation, at the same time as the acid precipitation, after the acid precipitation and before the redispersion, at the same time as the redispersion, or after the redispersion, and preferably before the acid precipitation or after the redispersion, and the present invention has thus been accomplished.

[0015]

That is, the present invention provides

1. a process for producing an aqueous pigment dispersion, the process comprising:
a step (1), using a pigment (A) and a resin (B) having a carboxyl group and a cross-linkable functional group, of precipitating the resin (B) so as to make it adhere to

the pigment (A) by making the pH of a pigment aqueous dispersion (1a) neutral or acidic using an acidic compound (E), the pigment aqueous dispersion (1a) being formed by neutralizing the carboxyl group of the resin (B) with a basic compound (F1) so as to make it hydrophilic;

a subsequent step (2) of redispersing in an aqueous medium the pigment to which the resin (B) is adhered by neutralizing the carboxyl group of the resin (B) using a basic compound (F2); and

adding a cross-linking agent (C) at any time,

wherein the cross-linkable functional group of the resin (B) and the cross-linking agent (C) are cross-linked at any time after the pigment aqueous dispersion (1a) is obtained,

[0016]

2. the production process according to the above-mentioned 1 wherein as the pigment aqueous dispersion (1a) there is used a pigment aqueous dispersion obtained by kneading the pigment (A) and the resin (B) in an organic solvent medium, adding the cross-linking agent (C) before or after the kneading, at least partly neutralizing the carboxyl group of the resin (B) using the basic compound (F1) before and/or after the kneading, and dispersing in an aqueous medium,

3. the production process according to the above-mentioned 1 wherein as the pigment aqueous dispersion (1a) there used is a pigment aqueous dispersion obtained by mixing and/or kneading the pigment (A), the resin (B) whose carboxyl group has been neutralized using the basic compound (F1), and the cross-linking agent (C) in an aqueous medium,

[0017]

4. the production process according to any one of the above-mentioned 1, 2, or 3 wherein the resin (B) is a vinyl-based copolymer, a polyester resin, or a polyurethane resin,

5. the production process according to any one of the above-mentioned 1, 2, 3, or 4 wherein the acid value based on the carboxyl group of the resin (B) is in the range of 30 to 120 mg KOH/g of resin solids content,

6. the production process according to any one of the above-mentioned 1, 2, 3, 4, or 5 wherein the cross-linkable functional group of the resin (B) is a carboxyl group and the cross-linking agent (C) is a cross-linking agent selected from the group consisting of an amino resin and a compound having at least two epoxy groups in one molecule, or the cross-linkable functional group of the resin (B) is a hydroxyl group and the cross-linking agent (C) is an amino resin,

7. the production process according to any one of the above-mentioned 1 to 6 wherein the cross-linkable functional group of the resin (B) and the cross-linking agent (C) are cross-linked before the acidic compound (E) is added or after the pigment (A) to which the resin (B) is adhered is redispersed in the aqueous medium,

[0018]

8. a process for producing an aqueous pigment dispersion, the process comprising:

a step (1), using a pigment (A) and a resin (D) having a carboxyl group and a self cross-linkable functional group, of precipitating the resin (D) so as to make it adhere to the pigment (A) by making the pH of a pigment aqueous dispersion (1b) neutral or acidic using an acidic compound (E), the pigment aqueous dispersion (1b) being formed by neutralizing the carboxyl group of the resin (D) with a basic compound (F1) so as to make it hydrophilic; and

a subsequent step (2) of redispersing in an aqueous medium the pigment (A) to which the resin (D) is adhered by neutralizing the carboxyl group of the resin (D) using a basic compound (F2);

wherein the resin (D) is self cross-linked at any time after the pigment aqueous dispersion (1b) is obtained,

[0019]

9. the production process according to the above-mentioned 8 wherein as the pigment aqueous dispersion (1b) there is used a pigment aqueous dispersion (1b) obtained by kneading the pigment (A) and the resin (D) in an organic solvent medium and at least partly neutralizing the carboxyl group of the resin (D) using the basic compound (F1) before the kneading and/or after the kneading, and dispersing in an aqueous medium,

10. the production process according to the above-mentioned 8 wherein as the pigment aqueous dispersion (1b) there is used a pigment aqueous dispersion (1b) obtained by mixing and/or kneading in an aqueous medium the pigment (A) and the resin (D) whose carboxyl group has been neutralized using the basic compound (F1),

[0020]

11. the production process according to any one of the above-mentioned 8, 9, or 10 wherein the resin (D) is a vinyl-based copolymer, a polyester resin, or a polyurethane resin,

12. the production process according to any one of the above-mentioned 8, 9, 10, or 11 wherein the acid value based on the carboxyl group of the resin (D) is in the range of 30 to 120 mg KOH/g of resin solids content,

13. the production process according to any one of the above-mentioned 8, 9, 10, 11 or 12 wherein the self cross-linkable functional group of the resin (D) is (1) one with a carboxyl group and an epoxy group in one molecule, (2) one with a hydroxyl group and an N-alkoxymethylamide group in one molecule, or (3) a radically polymerisable unsaturated group,

14. the production process according to any one of the above-mentioned 8 to 13 wherein the resin (D) is self cross-linked before the acidic compound (E) is added or after the pigment (A) to which the resin (D) is adhered is redispersed in the aqueous medium, and

[0021]

15. an aqueous colouring agent composition characterized in that it comprises an aqueous pigment dispersion produced by the production process according to any one of the above-mentioned 1 to 14.

[0022]

The acid value referred to in the present invention is represented by the amount of potassium hydroxide in mg necessary to neutralize 1 g of the resin solids content.

[0023]

The production process of the present invention can be broadly divided into a production process (I) according to the above-mentioned 1 to 7 and a production process

(II) according to the above-mentioned 8 to 14, and the production process (I) consists basically of the following production steps.

[0024]

Step (I-1): Using the pigment (A) and the resin (B) having a carboxyl group and a cross-linkable functional group, the carboxyl group of the resin (B) is neutralized with the basic compound (F1) so as to make it hydrophilic to form the pigment aqueous dispersion (1a), and the resin (B) is precipitated by making the pH of the pigment aqueous dispersion (1a) neutral or acidic using the acidic compound (E) so as to make the resin (B) adhere to the pigment (A).

Step (I-2): After the resin (B) is adhered to the pigment (A) in step (I-1), the carboxyl group of the resin (B) is neutralized using the basic compound (F2) so as to redisperse in the aqueous medium the pigment (A) to which the resin (B) is adhered.

Step (I-3): The cross-linking agent (C) is added, and subsequently in any stage after the water (sic.) pigment aqueous dispersion (1a) is obtained, the cross-linkable functional group of the resin (B) and the cross-linking agent (C) are cross-linked.

[0025]

The production process (II) of the present invention consists basically of the following steps.

Acid precipitation step (II-1): Using the pigment (A) and the resin (D) having a carboxyl group and a self cross-linkable functional group, the carboxyl group of the resin (D) is neutralized with the basic compound (F1) so as to make it hydrophilic to form the pigment aqueous dispersion (1b), and the resin (D) is precipitated by making the pH of the pigment aqueous dispersion (1b) neutral or acidic using the acidic compound (E) so as to make the resin (D) adhere to the pigment (A).

Step (II-2): After the resin (D) is adhered to the pigment (A) in step (II-1), the carboxyl group of the resin (D) is neutralized using the basic compound (F2) so as to redisperse in the aqueous medium the pigment (A) to which the resin (D) is adhered.

Step (II-3): At any stage after the pigment aqueous dispersion (1b) is obtained, the resin (D) is self cross-linked.

[0026]

In the above-mentioned production processes (I) and (II), the resin (B) or (D) may be cross-linked at any time as long as it is after the pigment aqueous dispersion (1a) or (1b) is obtained; for example,

- (1) during Step (I-1) or (II-1), after the pigment aqueous dispersion (1a) or (1b) is obtained, before the acidic compound (E) is added;
- (2) during Step (I-1) or (II-1), when the resin (B) or (D) is precipitated so as to adhere to the pigment (A) using the acidic compound (E),
- (3) after completion of Step (I-1) or (II-1), during Step (I-2) or (II-2), before the basic compound (F2) is added,
- (4) during Step (I-2) or (II-2), when the pigment (A) to which the resin (B) or (D) adheres is redispersed in the aqueous medium using the basic compound (F2),
- (5) in Step (I-2) or (II-2) after the pigment (A) to which the resin (B) or (D) adheres is redispersed in the aqueous medium, etc.

Among these, since a good aqueous pigment dispersion can be obtained, it is preferable to cross-link at the time of the above-mentioned (1) or (5), and it is most preferable to cross-link at the time of the above-mentioned (5). Furthermore, if cross-linking is carried out in the above-mentioned stage (2) or (4), there is the advantage that the step can be rationalized.

[0027]

The resin (B) or (D) used in the production process of the present invention may be any resin as long as it has a carboxyl group and a cross-linkable functional group or a self cross-linkable functional group. Examples thereof include vinyl-based copolymers, polyester resins, polyurethane resins, epoxy resins, and rosin-modified resins. Among these, vinyl-based copolymers, polyester resins, and polyurethane resins are preferable from the viewpoint of ease of introduction of the carboxyl group, ease of introduction of the cross-linkable functional group or the self cross-linkable functional group, and toughness of a coating.

[0028]

With regard to the vinyl-based copolymers used in the production process of the present invention, examples thereof include (meth)acrylate resins, (meth)acrylate-styrene copolymer resins, styrene-maleic acid (anhydride) copolymer resins, and

fluorine-containing vinyl-based copolymer resins. With regard to the polyester resins used in the production process of the present invention, examples thereof include saturated polyester resins, unsaturated polyester resins, and alkyd resins. It is essential for these resins to have a carboxyl group as a hydrophilic group for imparting an adequate degree of water solubility or water dispersibility and a cross-linkable functional group or a self cross-linkable functional group for cross-linking.

[0029]

The cross-linkable functional group is a functional group that can form a cross-linked bond by reacting with a cross-linking agent, and the self cross-linkable functional group is a functional group that can self cross-link and functional groups that can cross-bond.

[0030]

With regard to the cross-linkable functional group, examples thereof include a carboxyl group, a hydroxyl group, a tertiary amino group, a blocked isocyanate group, an epoxy group, and a 1,3-dioxolan-2-on-4-yl group.

[0031]

Representative examples of combinations of the cross-linkable functional group and the cross-linking agent (C) are listed below.

(a) In the case where the cross-linkable functional group is a carboxyl group, there can be cited as the cross-linking agent (C) an amino resin, a compound having at least two epoxy groups in one molecule, a compound having at least two 1,3-dioxolan-2-on-4-yl groups (also called cyclocarbonate groups) in one molecule, etc.

(b) In the case where the cross-linkable functional group is a hydroxyl group, there can be cited as the cross-linking agent (C) an amino resin, a polyisocyanate compound, a blocked polyisocyanate compound, etc.

(c) In the case where the cross-linkable functional group is a tertiary amino group, there can be cited as the cross-linking agent (C) a compound having at least two epoxy groups in one molecule, a compound having at least two 1,3-dioxolan-2-on-4-yl groups in one molecule, etc.

(d) In the case where the cross-linkable functional group is a blocked isocyanate group, there can be cited as the cross-linking agent (C) a compound having at least two hydroxyl groups in one molecule, etc.

(e) In the case where the cross-linkable functional group is an epoxy group or a 1,3-dioxolan-2-on-4-yl group, there can be cited as the cross-linking agent (C) a compound having at least two carboxyl groups in one molecule, a polyamine compound, a polymercapto compound, etc.

[0032]

With regard to the self cross-linkable functional group, examples thereof include a radically polymerisable unsaturated group and a hydrolysable alkoxysilane group. In order to reinforce the self cross-linking properties, a combination in which part is a compound having at least two radically polymerisable unsaturated groups and part is a compound having a hydrolysable alkoxysilane group can be used.

[0033]

The functional groups that can cross-bond are a combination in one molecule of at least two types of functional groups that can react. Examples of combinations of such functional groups include (a) a carboxyl group and an epoxy group, (b) a carboxyl group and a 1,3-dioxolan-2-on-4-yl group, (c) a hydroxyl group and a blocked isocyanate group, (d) a hydroxyl group and an N-alkoxymethylamide group, and (e) a hydroxyl group and a hydrolysable alkoxysilane group.

[0034]

A specific method for introducing the cross-linking and self cross-linkable functional groups to a resin is now described.

[0035]

The vinyl-based copolymer having a carboxyl group as the hydrophilic group and the cross-linkable functional group can be easily produced by a method in which a polymerisable monomer composition containing a polymerisable monomer having a carboxyl group is copolymerised. Examples of the polymerisable monomer having a carboxyl group include acrylic acid, methacrylic acid, crotonic acid, fumaric acid, itaconic acid, maleic acid (anhydride), monoalkyl maleates such as monobutyl maleate, and monoalkyl itaconates such as monobutyl itaconate.

[0036]

With regard to polymerisable vinyl monomers other than the polymerisable vinyl monomer having a carboxyl group contained in the polymerisable monomer composition, examples thereof include aromatic vinyl monomers such as styrene, vinyl toluene, and α -methylstyrene; (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, *n*-butyl (meth)acrylate, isobutyl (meth)acrylate, *tert*-butyl (meth)acrylate, isoamyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl (meth)acrylate, butoxymethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, cetyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, and isobornyl (meth)acrylate; vinyl esters such as vinyl acetate, vinyl benzoate, vinyl versatate, and vinyl propionate; polymerisable nitriles such as (meth)acrylonitrile; vinyl monomers having a fluorine atom such as vinyl fluoride, vinylidene fluoride, tetrafluoroethylene, hexafluoropropylene, and chlorotrifluoroethylene; tertiary amino group-containing monomers such as diethylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, N-vinylimidazole, and N-vinylcarbazole; monomers having UV absorbability or antioxidation properties such as 2-(2'-hydroxy-5-methacryloyloxyethylphenyl)-2H-benzotriazole, 2-hydroxy-4-(2-methacryloyloxyethoxy)benzophenone, and 1,2,2,6,6-pentamethyl-4-piperidyl methacrylate; monomers containing a functional group such as N-vinylpyrrolidone, glycidyl (meth)acrylate, 1,3-dioxolan-2-ylmethyl (meth)acrylate, 1,3-dioxolan-2-on-4-ylmethyl vinyl ether, diacetoneacrylamide, N-methylolacrylamide, and N-alkoxy methyl (meth)acrylamides including N-butoxymethyl (meth)acrylamide; phosphoric acid group-containing monomers such as 2-phosphooxyethyl (meth)acrylate, and 4-phosphooxybutyl (meth)acrylate; and macromonomers having one polymerisable unsaturated group at the molecular terminal.

[0037]

With regard to the method for polymerising the polymerisable vinyl monomer composition, various known polymerisation methods such as suspension polymerisation, emulsion polymerisation, bulk polymerisation, and solution polymerisation can be employed, and solution polymerisation is preferable for

simplicity. As a polymerisation initiator, a known peroxide or azo compound can be used.

[0038]

The vinyl-based copolymer having a carboxyl group can also be produced by a method in which a vinyl-based copolymer having a hydroxyl group, which will be described later, is subjected to an addition reaction with an acid anhydride such as maleic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, or trimellitic anhydride.

[0039]

The vinyl-based copolymer having a hydroxyl group and a carboxyl group can easily be produced by the combined use of a polymerisable monomer having a hydroxyl group when the above-mentioned vinyl copolymer having a carboxyl group is produced. With regard to the polymerisable monomer having a hydroxyl group, examples thereof include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, (meth)acrylic monomers to which a lactone compound has been added represented by 'Placel FM-2' and 'Placel FA-2' (manufactured by Daicel Chemical Industries, Ltd.), polyethylene glycol mono(meth)acrylate monomers, polypropylene glycol mono(meth)acrylate monomers, hydroxyethyl vinyl ether, and hydroxybutyl vinyl ether.

[0040]

The vinyl-based copolymer having a tertiary amino group and a carboxyl group can easily be produced by the combined use of a polymerisable monomer having a tertiary amino group when the above-mentioned vinyl copolymer having a carboxyl group is produced. With regard to the polymerisable monomer having a tertiary amino group, examples thereof include diethylaminoethyl (meth)acrylate and dimethylaminoethyl (meth)acrylate.

[0041]

The vinyl copolymer having a blocked isocyanate group and a carboxyl group can easily be produced by the combined use of a polymerisable monomer having a blocked isocyanate group when the above-mentioned vinyl-based copolymer having a carboxyl group is produced.

[0042]

The polymerisable monomer having a blocked isocyanate group can easily be produced by adding a known blocking agent to a polymerisable monomer having an isocyanate group such as 2-methacryloyloxyethyl isocyanate. Alternatively, it can easily be produced by adding a compound having an isocyanate group and a blocked isocyanate group to the above-mentioned vinyl-based copolymer having a hydroxyl group and a carboxyl group.

[0043]

The compound having an isocyanate group and a blocked isocyanate group can easily be produced by subjecting a diisocyanate compound and a known blocking agent to an addition reaction at a molar ratio of about 1:1.

[0044]

The vinyl-based copolymer having an epoxy group and a carboxyl group can easily be produced by the combined use of a polymerisable monomer having an epoxy group when the above-mentioned vinyl copolymer having a carboxyl group is produced. With regard to the polymerisable monomer having an epoxy group, examples thereof include glycidyl (meth)acrylate and (meth)acrylate monomers having an alicyclic epoxy group.

[0045]

The vinyl-based copolymer having a 1,3-dioxolan-2-on-4-yl group and a carboxyl group can easily be produced by the combined use of a polymerisable monomer having a 1,3-dioxolan-2-on-4-yl group when the above-mentioned vinyl copolymer having a carboxyl group is produced. With regard to the polymerisable monomer having a 1,3-dioxolan-2-on-4-yl group, examples thereof include 1,3-dioxolan-2-on-4-ylmethyl (meth)acrylate and 1,3-dioxolan-2-on-4-ylmethyl vinyl ether.

[0046]

The vinyl-based copolymer having a polymerisable unsaturated group as a self cross-linkable functional group and a carboxyl group can easily be produced by, for example, a method (a) in which an addition reaction of a polymerisable monomer having a tertiary amino group to a vinyl-based copolymer having an epoxy group and a

carboxyl group is carried out, a method (b) in which an addition reaction of a polymerisable monomer having an isocyanate group such as 2-methacryloyloxyethyl isocyanate or an acid anhydride having a polymerisable unsaturated group such as maleic anhydride to a vinyl-based copolymer having a hydroxyl group and a carboxyl group is carried out, or a method (c) in which an addition reaction of a polymerisable monomer having an epoxy group to a vinyl-based copolymer having a carboxyl group is carried out.

[0047]

The vinyl-based copolymer having a cross-reactive functional group and a carboxyl group can easily be produced, when the above-mentioned vinyl copolymer having a carboxyl group is produced, by copolymerising a polymerisable monomer having a cross-reactive functional group such as (a) a polymerisable monomer having an epoxy group, (b) a polymerisable monomer having a 1,3-dioxolan-2-on-4-yl group, or a combination such as (c) a polymerisable monomer having a hydroxyl group and a polymerisable monomer having a blocked isocyanate group, or (d) a polymerisable monomer having a hydroxyl group and a polymerisable monomer having an N-alkoxymethylamide group.

[0048]

The polyester resin having a carboxyl group as the hydrophilic group and the cross-linkable functional group is produced by carrying out a dehydration-condensation reaction between a compound having a carboxyl group and a compound having a hydroxyl group by a known method such as a melt method or a solvent method so that carboxyl group remains.

[0049]

The polyester resin can be obtained by a dehydration-condensation between a compound having a carboxyl group such as a monobasic acid, a dibasic acid, or a polybasic acid and a compound having a hydroxyl group such as a diol or a polyol in an appropriate combination. When a fat or oil, or a fatty acid is used, an alkyd resin is obtained.

[0050]

The carboxyl group of the polyester resin used in the production process of the present invention is mainly an unreacted carboxyl group originating from a dibasic acid or a polybasic acid that constitutes the polyester resin.

[0051]

Examples of the dibasic acid or polybasic acid include adipic acid, succinic acid (anhydride), sebacic acid, dimer acid, maleic acid (anhydride), phthalic acid (anhydride), isophthalic acid, terephthalic acid, tetrahydrophthalic acid (anhydride), hexahydrophthalic acid (anhydride), hexahydroterephthalic acid, 2,6-naphthalenedicarboxylic acid, trimellitic acid (anhydride), and pyromellitic acid (anhydride).

[0052]

With regard to a compound having a carboxyl group that can be used, other than the dibasic acid or the polybasic acid, examples thereof include lower alkyl esters of acids such as dimethyl terephthalate; monobasic acids such as benzoic acid, *p*-tertiary butylbenzoic acid, rosin, and hydrogenated rosin; fatty acids and fats and oils; macromonomers having one or two carboxyl groups at their molecular terminals; and 5-sodium sulphoisophthalic acid and dimethyl esters thereof.

[0053]

With regard to the compound having a hydroxyl group, examples thereof include diols such as ethylene glycol, neopentyl glycol, propylene glycol, diethylene glycol, dipropylene glycol, 2-methyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,4-butanediol, 1,3-propanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, 1,5-pentanediol, alkylene oxide adducts of bisphenol A, hydrogenated bisphenol A, alkylene oxide adducts of hydrogenated bisphenol A, polyethylene glycol, polypropylene glycol, and polytetramethylene glycol; polyols such as glycerol, trimethylolpropane, trimethylolethane, diglycerol, pentaerythritol, and trishydroxyethyl isocyanurate; monoglycidyl compounds such as 'Cardura E-10' (the glycidyl ester of a synthetic fatty acid; manufactured by Shell Chemical Industries), and macromonomers having two hydroxyl groups at their molecular terminals.

[0054]

When synthesizing the polyester resin, a hydroxyl group-containing fatty acid or fat or oil such as castor oil or 12-hydroxystearic acid; a compound having a carboxyl group and a hydroxyl group such as dimethylolpropionic acid or p-hydroxybenzoic acid; a cyclic ester compound such as ϵ -caprolactone; etc. can be used.

[0055]

Furthermore, a portion of the dibasic acid may be replaced with a diisocyanate compound.

[0056]

Moreover, the polyester resin having a carboxyl group can also be produced by a method in which an addition reaction of an acid anhydride such as maleic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, or trimellitic anhydride to a polyester resin having a hydroxyl group is carried out.

[0057]

The polyester resin having a hydroxyl group and a carboxyl group can be produced easily in a dehydration-condensation reaction of a polyester resin by carrying out the reaction by a known method so that hydroxyl group and carboxyl group remain.

[0058]

The polyester resin having a tertiary amino group and a carboxyl group can be produced easily by using a compound having a tertiary amino group and a hydroxyl group such as triethanolamine, N-methyldiethanolamine or N,N-dimethylethanolamine as the alcohol component when producing the polyester resin.

[0059]

The polyester resin having a polymerisable unsaturated group as a self cross-linkable functional group and a carboxyl group can be produced easily by a method (a) in which an addition reaction of a polymerisable monomer having an isocyanate group such as 2-methacryloyloxyethyl isocyanate, or an acid anhydride having a polymerisable unsaturated group such as maleic anhydride to a polyester resin having a hydroxyl group and a carboxyl group is carried out, a method (b) in which an addition reaction of a polymerisable monomer having an epoxy group such as one described above to a polyester resin having a carboxyl group is carried out, or a method (c) in which a

polyester is synthesized using a polymerisable unsaturated group such as maleic anhydride as the acid component.

[0060]

The polyurethane resin having a carboxyl group used in the production process of the present invention can be produced easily by reacting a polyisocyanate component with, as a component for introducing a carboxyl group, a polyol component containing a compound having a carboxyl group and a hydroxyl group, such as dimethylolpropionic acid.

[0061]

As the polyol component, in addition to the diol component cited in the production process for a polyester, a tri- or higher functional polyol compound can be used as necessary.

[0062]

As the polyisocyanate component, there can be used a diisocyanate compound such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, phenylene diisocyanate, 1,5-naphthalene diisocyanate, metaxylylene diisocyanate, isophorone diisocyanate, hydrogenated tolylene diisocyanate, hydrogenated 4,4'-diphenylmethane diisocyanate, hydrogenated metaxylylene diisocyanate, or crude 4,4'-diphenylmethane diisocyanate, and also a polyisocyanate compound such as polymethylene polyphenyl isocyanate.

[0063]

The polyurethane resin can be produced by a standard method. For example, an addition reaction is preferably carried out in an inert organic solvent solution that does not react with an isocyanate group, at room temperature or at a temperature of on the order of 40 to 100°C. In this process, a known catalyst such as dibutyl tin dilaurate may be used.

[0064]

The reaction system for producing the polyurethane resin can employ a known chain extending agent such as a diamine, a polyamine, an N-alkyldialkanolamine such as N-methyldiethanolamine; or a dihydrazide compound.

[0065]

A polyurethane resin having a hydroxyl group and a carboxyl group can easily be produced by carrying out a reaction with a higher proportion of hydroxyl group than of isocyanate group when producing the polyurethane resin. Alternatively, it can easily be produced by an addition reaction of a compound having at least two hydroxyl groups in one molecule to a polyisocyanate resin having a carboxyl group and a terminal isocyanate group.

[0066]

A polyurethane resin having a tertiary amino group and a carboxyl group can easily be produced using an N-alkyldialkanolamine such as N-methyldiethanolamine as part of the polyol component.

[0067]

A polyurethane resin having a blocked isocyanate group and a carboxyl group can easily be produced by an addition reaction of a known blocking agent to a polyisocyanate resin having a carboxyl group and a terminal isocyanate group.

[0068]

A polyurethane resin having an epoxy group and a carboxyl group can easily be produced by an addition reaction of a compound having a hydroxyl group and an epoxy group to a polyisocyanate resin having a carboxyl group and a terminal isocyanate group.

[0069]

With regard to the compound having a hydroxyl group and an epoxy group, examples thereof include glycidol, glycerol diglycidyl ether, trimethylolpropanediglycidyl ether, and the diglycidyl ether of bisphenol A.

[0070]

A polyurethane resin having a polymerisable unsaturated group as a self cross-linkable functional group and a carboxyl group can easily be produced by, for example, a method in which an addition reaction of the above-mentioned polymerisable monomers having a hydroxyl group and a compound having a hydroxyl group and a polymerisable unsaturated group such as glycerol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, or pentaerythritol triacrylate to a polyisocyanate resin having a terminal isocyanate group is carried out.

[0071]

A polyurethane resin having a hydrolysable alkoxysilane group as a self cross-linkable functional group and a carboxyl group can easily be produced by an addition reaction of a silane coupling agent having an active hydrogen that can react with an isocyanate group, such as γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -aminopropyltrimethoxysilane, or γ -aminopropyltriethoxysilane to a polyisocyanate resin having a terminal isocyanate group.

[0072]

The amount of carboxyl groups in the resin (B) having a carboxyl group and a cross-linkable functional group or the resin (D) having a carboxyl group and a self cross-linkable functional group is preferably an amount that gives an acid value of 30 to 120, and more preferably 50 to 100. If the acid value exceeds 120, then the hydrophilicity becomes too high, and the water resistance of coated material is greatly degraded. If the acid value is less than 30, then the redispersion in water after acid precipitation and neutralization becomes poor, which is undesirable.

[0073]

In the case where the resin (B) or resin (D) having a carboxyl group and a cross-linkable functional group or a self cross-linkable functional group is a vinyl-based copolymer or a polyurethane resin, one having a number average molecular weight of 5,000 to 20,000 is preferable. If the number average molecular weight is less than 5,000, when it is used in a coating agent, the coated material tends to become brittle. If the number average molecular weight is higher than 20,000, it becomes difficult to obtain a fine pigment dispersion, which is undesirable.

[0074]

In the case where the resin (B) or resin (D) having a carboxyl group and a cross-linkable functional group or a self cross-linkable functional group is a polyester resin, since most polyester resins are of a branched type, with regard to the molecular weight, unlike a linear vinyl-based copolymer, even if the number average molecular weight is small, the weight average molecular weight is large, and sufficient toughness as a coating can be obtained. The number average molecular weight of the polyester resin is

preferably in the range of 1,000 to 20,000, and the weight average molecular weight is preferably in the range of 5,000 to 100,000.

[0075]

The pigment (A) used in the present invention may be an inorganic pigment or an extender pigment, but carbon black and organic pigments are particularly preferable.

[0076]

Representative examples of the organic pigments include phthalocyanine pigments such as phthalocyanine blue, phthalocyanine green, hansa yellow and permanent red, anthraquinones, perinones, dioxazines, perylenes, quinacridones, azo type metal complexes, methine type metal complexes, thioindigos, isoindolinones, isoindolines, threnes, and diaminoanthraquinones.

[0077]

The pigment used in the present invention may be a powder or solidified, or in a state in which it is dispersed in water, such as an aqueous slurry or a press cake.

[0078]

The production steps in the present invention are now given in sequence.

[0079]

First, in a step of mixing or kneading the pigment and the resin (B) or resin (D) having a carboxyl group and a cross-linkable functional group or a self cross-linkable functional group, the following two methods are suitable.

Method (1): after the resin and the pigment are kneaded in an organic solvent medium, they are dispersed in an aqueous medium.

Method (2): the pigment is mixed or kneaded in an aqueous medium.

[0080]

In order to knead the resin and the pigment in the organic solvent in Method (1), first of all, the powdered or solid pigment and an organic solvent solution of the resin is finely kneaded using a known disperser such as a ball mill, a sand mill, or a colloid mill.

[0081]

As the organic solvent used in Method (1), all generally used solvents can be used, but those in which the resin has good solubility, give no problems in terms of synthesis of the resin, have a vapour pressure higher than that of water and are easily

removed, and are miscible with water are preferable. Examples of such organic solvents include acetone, methyl ethyl ketone, methanol, ethanol, *n*-propanol, isopropanol, ethyl acetate, and tetrahydrofuran. Although the miscibility with water is low, methyl isopropyl ketone, methyl *n*-propyl ketone, isopropyl acetate, *n*-propyl acetate, methylene chloride, benzene, etc. can also be used.

[0082]

In order to disperse in an aqueous medium a dispersion comprising the organic solvent, the resin, and the pigment, the carboxyl group of the resin is neutralized with a basic compound (F1) so as to make the resin hydrophilic, thus enabling it to be dispersed in water.

[0083]

With regard to the method for dispersing in water, the methods described below are suitable.

Method (a): a dispersion comprising the organic solvent, the pigment, and the resin is neutralized with the basic compound, and water is then added dropwise.

Method (b): water is added dropwise to a dispersion comprising the organic solvent, the pigment, and the resin, the resin having been neutralized using the basic compound.

Method (c): water containing the basic compound is added dropwise to a dispersion comprising the organic solvent, the pigment, and the resin.

Method (d): a dispersion comprising the organic solvent, the pigment, and the resin is neutralized with the basic compound, and is then added to the water medium.

Method (e): a dispersion comprising the organic solvent, the pigment, and the resin, the resin having been neutralized using the basic compound, is added to the water medium.

Method (f): a dispersion comprising the organic solvent, the pigment, and the resin is added to the water medium containing the basic compound.

[0084]

Dispersing in water may be carried out by ordinary stirring at low shear, stirring at high shear by means of a homogenizer, etc., or ultrasound. With the purpose of assisting dispersion in the aqueous medium, a surfactant, a protective colloid, etc. can be used in combination in a range that does not greatly degrade the water resistance of the coated material.

[0085]

Examples of the basic compound (F1) include inorganic bases such as sodium hydroxide and potassium hydroxide and organic amines such as ammonia, triethylamine, tributylamine, dimethylethanolamine, diisopropanolamine, and morpholine.

[0086]

In Method (2), in order to knead the resin and the pigment in the aqueous medium, after the carboxyl group of the resin is first neutralized using the above-mentioned basic compound (F1), it is mixed or kneaded with the pigment in the aqueous medium. During this process, the resin dissolved or dispersed in water may contain the organic solvent, or the medium may contain substantially only water as a result of carrying out solvent removal. The pigment used can be any of a powdered pigment, an aqueous slurry, and a press cake. During dispersion in the aqueous medium, in order to simplify the production step, it is preferable to use the aqueous slurry or the press cake since there is less secondary aggregation of pigment particles. The kneading method, the organic solvent, and the basic compound (F1) may be the same as those used for dispersing in the organic solvent medium.

[0087]

In the neutralization of the carboxyl group with the basic compound (F1) in order to make hydrophilic the resin (B) or resin (D) having a carboxyl group and a cross-linkable functional group or a self cross-linkable functional group, the resin may be made hydrophilic at least to an extent that the resin is hydrophilic enough to give the pigment aqueous dispersion (1a) or (1b), and it is unnecessary for all the carboxyl groups of the resin to be neutralized. Usually, about 50 to 100 mol % of the carboxyl groups of the resin are neutralized.

[0088]

In the case of kneading in either an organic solvent system or an aqueous system, in order to assist the dispersion of the pigment, a pigment dispersing agent or a wetting agent can be used in combination in a range that does not degrade the water resistance of the coated material.

[0089]

When kneading the pigment, or after kneading, a material other than the pigment, for example, a dye, an antioxidant, a UV absorbing agent, a cross-linking catalyst for a coating agent binder, a corrosion inhibitor, a perfume, a chemical agent, etc. can be added.

[0090]

With regard to the ratio of the resin to the pigment, it is preferable to use 1 to 200 parts by weight of the resin solids content relative to 100 parts by weight of the pigment, and particularly preferably 5 to 100 parts by weight. If the proportion of the resin solids content is less than 1 part by weight, then it tends to be difficult to disperse the pigment sufficiently finely. If it is more than 200 parts by weight, then the proportion of the pigment in the dispersion is small, and when it is used in a coating agent, etc., there tends to be no allowance in the design of the composition, which is undesirable.

[0091]

The acid precipitation, which is carried out in order to make the resin adhere strongly to the pigment that has been finely dispersed in the aqueous medium, is carried out by adding the acidic compound (E) to the carboxyl group, which has been neutralized with the basic compound (F1), so as to make the pH neutral or acidic, thus making the resin hydrophobic. Examples of the acidic compound (E) used include inorganic acids such as hydrochloric acid, sulphuric acid, phosphoric acid, and nitric acid; and organic acids such as formic acid, acetic acid, and propionic acid. An inorganic acid such as hydrochloric acid is preferable since the amount of organic material in the waste water is small and the acid precipitation effect is large. The pH is preferably in the range of 3 to 6, but in the case of a pigment that is decomposed by an acid, the acid precipitation can be carried out at a pH of 4 to 7. In addition, in the case where the resin or the cross-linking agent has an epoxy group, since hydrochloric acid or an organic acid reacts with the epoxy group they are not suitable as the acidic compound; in such a case phosphoric acid, etc. can be preferably used, and the pH is preferably on the order of 5 to 7. Before carrying out the acid precipitation, the organic solvent present in the system is preferably removed by vacuum distillation, etc.

[0092]

After the acid precipitation, a damp cake of dispersed pigment is produced by carrying out filtration and water-washing, as necessary. The filtration can be carried out by a known method such as suction filtration, pressure filtration, or centrifugation.

[0093]

By subjecting this damp cake, without drying and as it is in the damp state, to re-neutralization of the carboxyl group using the basic compound (F2), the pigment particles can be redispersed in the aqueous medium while maintaining them in a fine state without the particles aggregating. The basic compound (F2) is preferably ammonia or a volatile amine compound such as triethylamine or dimethylethanolamine when the water resistance of the coated material, etc. is taken into consideration.

[0094]

The cross-linking in the present invention is now explained.

[0095]

In the case where cross-linking is self cross-linking, cross-linking may be carried out in any state, that is, the water dispersion before acid precipitation, the damp cake after acid precipitation, and the aqueous dispersion re-neutralized with the basic compound (F2), but it is preferable to carry out cross-linking in the water dispersion state before acid precipitation or the aqueous dispersion state after re-neutralization, and it is more preferable to carry out cross-linking in the aqueous dispersion state after re-neutralization.

[0096]

Self cross-linking by means of a carboxyl group and an epoxy group, self cross-linking by means of a hydroxyl group and an N-alkoxymethylamide group, and self cross-linking by means of a hydrolysable alkoxysilane group can be carried out under the above-mentioned conditions, and in order to carry out the cross-linking more rapidly, a cross-linking catalyst can be used as appropriate.

[0097]

In the case of self cross-linking with a radically polymerisable unsaturated group, a water-soluble polymerisation initiator such as potassium persulphate or ammonium persulphate is added and, furthermore, the polymerisation is in a redox system, and cross-linking is carried out at a temperature of on the order of 50 to 90°C.

[0098]

On the other hand, in the case where cross-linking is carried out using the cross-linking agent (C), the cross-linking agent may be added to any of: the resin used, the aqueous dispersion before the acid precipitation, the damp cake after the acid precipitation, and the aqueous dispersion re-neutralized with the basic compound (F2), and cross-linking can also be carried out in any of: the water dispersion state before the acid precipitation, the damp cake state after the acid precipitation, and the aqueous dispersion state after re-neutralization. However, in order to obtain a finer aqueous dispersion of the pigment, the following cross-linking agent, mixing method, and cross-linking method are preferably employed.

[0099]

The cross-linking agent (C) can be of any type such as one that is infinitely soluble in water, one having moderate hydrophilicity, or one that is completely hydrophobic. One that is completely hydrophobic can be incorporated into the particles by mixing it with the resin (B) having a carboxyl group and a cross-linkable functional group, and dispersing in water.

[0100]

Among these cross-linking agents (C), a preferred cross-linking agent is not one that is infinitely soluble in water or one that is completely hydrophobic, but one having moderate hydrophilicity. When one that is infinitely soluble in water is used, since a part of the cross-linking agent dissolves in the aqueous medium, cross-linking between dispersed particles cannot be ignored, and there is a possibility that large particles might be formed. When one that is completely hydrophobic is used, it cannot be dispersed well in the aqueous medium, and there is still the possibility that large particles might be formed. The hydrophilicity of the cross-linking agent (C) of the present invention is preferably such that it has a water tolerance in the range of 10 to 2,000%, and more preferably 20 to 1,000%.

[0101]

The water tolerance referred to here is measured as follows.

[0102]

5 g of a resin solution is weighed in a 100 cc Erlenmeyer flask, ion-exchanged water is added dropwise while stirring at 25°C, and the amount of water that has been added when the liquid becomes cloudy and characters on a newspaper become impossible to read is expressed as a % relative to the resin. For example, if the ion-exchanged water is 10 cc, the water tolerance is 200%.

[0103]

With regard to the stage at which the cross-linking agent (C) is added, it is preferable to add it to the resin solution used before kneading with the pigment. In either the case in which a mixed solution of the resin (B) solution and the cross-linking agent (C) is used for kneading the pigment (A) in the organic solvent system and then dispersing it in water, or in the case in which the mixed solution is dispersed in water and the pigment (A) is then kneaded, the cross-linking agent (C) is in a state in which it is encapsulated by the resin (B) and is dispersed in water, and cross-linking proceeds entirely within particles, thus preventing the formation of large particles.

[0104]

The timing of the cross-linking may be any of the above as long as it is after the pigment aqueous dispersion (1a) is obtained, but cross-linking before adding the acidic compound (E) for carrying out the acid precipitation, or in the aqueous dispersion after re-neutralization is preferable, and cross-linking in the aqueous dispersion after re-neutralization is most preferable.

[0105]

The cross-linking is preferably carried out by heating under normal pressure at 50 to 100°C, but it is also possible to carry out cross-linking under increased pressure at on the order of 100 to 150°C in some cases. The use of a cross-linking catalyst can also be recommended.

[0106]

Examples of such a cross-linking agent (C) include amino resins, and compounds having at least two epoxy groups in one molecule.

[0107]

Representative examples of the amino resins include melamine resins, urea resins, and benzoguanamine resins, and they are converted into methylols by means of formaldehyde and then etherified with methanol or butanol.

[0108]

The compounds having at least two epoxy groups are, for example, various types of polyglycidyl ethers and polyglycidyl esters, which are called epoxy resins, and vinyl-based copolymers formed by copolymerising polymerisable monomers having an epoxy group, such as glycidyl methacrylate.

[0109]

The mixing ratio of the resin (B) to the cross-linking agent (C) is preferably approximately 50:50 to 95:5 as a solids content ratio, and particularly preferably 70:30 to 90:10.

[0110]

The aqueous pigment dispersion thus obtained preferably has a volume average particle size in the range of 10 to 500 nm. If the volume average particle size is larger than 500 nm, the gloss of coated material, the colouring properties, and the colouring power tend to be poor, which is undesirable. Making it less than 10 nm is very difficult and not practical.

[0111]

The aqueous pigment dispersion thus obtained is used by adding it to various aqueous colouring agent compositions such as, for example, a water-based paint, a water-based ink, and a printing agent.

[0112]

[Examples]

The present invention is explained further in detail below by reference to Examples, but the present invention is not limited by the scope of these Examples. In addition, 'parts' and '%' in the Examples below denote 'parts by weight' and 'wt %' respectively unless otherwise noted.

[0113]

The molecular weight in the present invention was measured by GPC (Gel Permeation Chromatography), and the volume average particle size was measured using

a 'UPA-150' (Laser-Doppler type particle size distribution analyser manufactured by Nikkiso Co., Ltd.).

[0114]

(Synthesis Example 1)

[Synthesis of vinyl-based copolymer having carboxyl group and hydroxyl group]

A 3L four neck flask equipped with a dropping device, a thermometer, a nitrogen gas inlet tube, a stirrer, and a reflux condenser was charged with 1,000 parts of methyl ethyl ketone, it was heated to 78°C, a liquid mixture consisting of 100 parts of styrene, 538 parts of *n*-butyl methacrylate, 104 parts of *n*-butyl acrylate, 150 parts of 2-hydroxyethyl methacrylate, 108 parts of methacrylic acid, and 80 parts of tertiary butyl peroxy-2-ethylhexanoate ('Perbutyl O' manufactured by NOF Corporation) was then added dropwise over 4 hours, and they were reacted at the same temperature for 8 hours. After the reaction was complete, methyl ethyl ketone was added so as to adjust the nonvolatile content to 50%, thus giving a resin solution A having an acid value of 70 for the resin solids content (hereinafter, the acid value is expressed as the value for the resin solids content), and a number average molecular weight of 6,000.

[0115]

(Synthesis Example 2)

[Synthesis of vinyl-based copolymer having carboxyl group and hydroxyl group]

The procedure of Synthesis Example 1 was repeated except that the monomers and the polymerisation initiator used were 100 parts of styrene, 454 parts of *n*-butyl methacrylate, 143 parts of *n*-butyl acrylate, 150 parts of 2-hydroxyethyl methacrylate, 153 parts of methacrylic acid, and 20 parts of tertiary butyl peroxy-2-ethylhexanoate, and a resin solution B having an acid value of 100 for the resin solids content and a number average molecular weight of 16,000 was obtained.

[0116]

(Synthesis Example 3)

[Synthesis of vinyl-based copolymer having carboxyl group and epoxy group]

The procedure of Synthesis Example 1 was repeated except that the monomers and the polymerisation initiator used were 100 parts of styrene, 476 parts of *n*-butyl methacrylate, 116 parts of *n*-butyl acrylate, 150 parts of 2-hydroxyethyl methacrylate, 50

parts of glycidyl methacrylate, 108 parts of methacrylic acid, and 80 parts of tertiary butyl peroxy-2-ethylhexanoate, and a resin solution C having an acid value of 70 for the resin solids content and a number average molecular weight of 10,500 was obtained.

[0117]

(Synthesis Example 4)

[Synthesis of vinyl-based copolymer having carboxyl group and N-butoxymethylamide group]

The procedure of Synthesis Example 1 was repeated except that 800 parts of methyl ethyl ketone and 200 parts of isopropyl alcohol were used instead of 1,000 parts of methyl ethyl ketone, and the monomers and the polymerisation initiator used were 100 parts of styrene, 459 parts of *n*-butyl methacrylate, 83 parts of *n*-butyl acrylate, 150 parts of 2-hydroxyethyl methacrylate, 100 parts of N-butoxymethyl methacrylamide, 108 parts of methacrylic acid, and 80 parts of tertiary butyl peroxy-2-ethylhexanoate, and a resin solution D having an acid value of 70 for the resin solids content and a number average molecular weight of 8,000 was obtained.

[0118]

(Synthesis Example 5)

[Synthesis of vinyl-based copolymer having polymerisable unsaturated group]

A 3L four neck flask equipped with a dropping device, a thermometer, a nitrogen gas inlet tube, a stirrer, and a reflux condenser was charged with 190 parts of the resin solution A obtained in Synthesis Example 1, 5 parts of 2-methacryloyloxyethyl isocyanate, and 0.05 parts of 'Suwanox BHT' (a polymerisation inhibitor manufactured by Seiko Chemical Industries Co., Ltd.), and they were reacted at 70°C for 3 hours. After the reaction was complete, methyl ethyl ketone was added so as to adjust the nonvolatile content to 50%, thus giving a resin solution E having an acid value of 67 for the resin solids content and a number average molecular weight of 7,000.

[0119]

(Synthesis Example 6)

[Synthesis of polyester resin having carboxyl group and hydroxyl group]

A 2L four neck flask equipped with a water removal tube, a thermometer, a nitrogen gas inlet tube, and a stirrer was charged with 100 parts of 'Cardura E-10' (the

glycidyl ester of a synthetic fatty acid, manufactured by Shell Chemical Industries), 241 parts of adipic acid, 376 parts of hexahydrophthalic anhydride, 195 parts of neopentyl glycol, 165 parts of trimethylolpropane, and 0.5 parts of a dibutyl tin dioxide, and heated to 190°C over 5 hours while removing water, and a dehydration-condensation reaction was then carried out at the same temperature. The acid value was measured by sampling, the reaction was completed when a target acid value of 60 was achieved, the mixture was cooled, and the mixture was diluted with methyl ethyl ketone so that the nonvolatile content was 65%. A resin solution F having an acid value of 61, a number average molecular weight of 2,200, a weight average molecular weight of 30,000, and a hydroxyl group value per equivalent of resin solids content of 60 was obtained.

[0120]

(Synthesis Example 7)

[Synthesis of polyurethane resin having carboxyl group]

A 3L four neck flask equipped with a thermometer, a nitrogen gas inlet tube, a stirrer, and a reflux condenser was charged with 900 parts of methyl ethyl ketone, 129 parts of dimethylolpropionic acid, 521 parts of 'Placel 212' (a polylactonediol manufactured by Daicel Chemical Industries, Ltd.) and 350 parts of isophorone diisocyanate, after they were reacted at 78°C for 2 hours, 0.1 parts of dibutyl tin dilaurate was added, and they were reacted at the same temperature for a further 4 hours. After the reaction was complete, the reaction mixture was cooled to 30°C, a solution consisting of 5.8 parts of ethylenediamine and 106 parts of methyl ethyl ketone was added, and a reaction was carried out for 1 hour, thus giving a resin solution G having an acid value of 54 and a number average molecular weight of 12,000.

[0121]

(Example 1)

(1) Pigment dispersion step of kneading pigment in aqueous medium

12.8 parts of the resin solution A (6.4 parts as solids content) was neutralized using 0.71 parts of dimethylethanolamine, and then mixed with 2.29 parts (1.6 parts as solids content) of 'Nikarack MX-041' (a methoxylated melamine resin, manufactured by Sanwa Chemical Co., Ltd.). To this mixed solution was added while stirring 50 parts of an aqueous slurry with a pigment content of 16% (8 parts as pigment content) of

'Fastogen Super Maroon PSK' (a cyanine blue pigment, manufactured by Dainippon Ink & Chemicals, Inc.).

[0122]

(2) Acid precipitation step

To the dispersed sample was added water (in the present specification, ion-exchanged water was used in all cases) to dilute it by a factor of two, and a 1N aqueous solution of hydrochloric acid was added while stirring by means of a Disper until the resin became insoluble and adhered to the pigment. The pH at this stage was approximately 3 to 5.

[0123]

(3) Filtration and water-washing step

The pigment to which the resin was adhered was suction-filtered, and then water-washed with ion-exchanged water until the pH of the washing exceeded 6, to give a damp cake.

[0124]

(4) Neutralization and redispersion in aqueous medium step

Water was added to the damp cake until it became fluid, a 10% aqueous solution of dimethylethanolamine was added until the pH of the dispersion became 8.5 to 9.5 while stirring by means of a Disper, and the stirring was then continued for 1 hour in that state. Water was added to the redispersion to adjust the nonvolatile content to 20%.

[0125]

(5) Cross-linking step

To the redispersion, 'Nacure 2500X' (a cross-linking catalyst manufactured by Kusumoto Chemicals, Ltd.) was added at 0.5% relative to the resin solids content, a cross-linking reaction was carried out at 95°C for 1 hour, and an aqueous pigment dispersion (A-1) was obtained.

[0126]

(Comparative Example 1)

To a solution in which 16 parts (8 parts as solids content) of the resin solution A had been neutralized using 0.80 parts of dimethylethanolamine, 50 parts of an aqueous slurry with a pigment content of 16% (8 parts as pigment content) of 'Fastogen Super

Maroon PSK' was added while stirring, and the solvent was then removed. Water was added thereto to adjust the nonvolatile content to 20%, and an aqueous pigment dispersion (a-1) was obtained.

[0127]

(Comparative Example 2)

To a solution in which 16 parts (8 parts as solids content) of the resin solution A had been neutralized using 0.80 parts of dimethylethanolamine, 50 parts of an aqueous slurry with a pigment content of 16% (8 parts as pigment content) of 'Fastogen Super Maroon PSK' was added while stirring, water was then added to the dispersed sample so as to dilute it by a factor of two, and a 1N aqueous solution of hydrochloric acid was added while stirring by means of a Disper until the resin became insoluble and adhered to the pigment. The pH at this stage was approximately 3 to 5.

[0128]

Next, the pigment to which the resin was adhered was suction-filtered, then water-washed with ion-exchanged water until the pH of the washing exceeded 6, to give a damp cake.

[0129]

Water was added to the damp cake until it became fluid, a 10% aqueous solution of dimethylethanolamine was added until the pH of the dispersion became 8.5 to 9.5 while stirring by means of a Disper, and the stirring was then continued for 1 hour in that state. Water was added to the redispersion to adjust the nonvolatile content to 20%, and an aqueous pigment dispersion (a-2) was obtained.

[0130]

(Comparative Example 3)

The procedure of Example 1 was repeated except that, after the dispersed sample obtained in the pigment dispersion step of Example 1 was subjected to solvent removal, cross-linking was carried out, and an aqueous pigment dispersion (a-3) was obtained.

[0131]

(Example 2)

(1) Pigment dispersion step

A 250 cc glass bottle was charged with 14.4 parts (7.2 parts as solids content) of the resin solution B, 8 parts of 'Fastogen Super Maroon PSK' powder, and 40 parts of methyl ethyl ketone together with 130 parts of glass beads having an average diameter of 1.5 mm, and kneading was carried out for 4 hours by means of a paint shaker.

[0132]

To this kneaded material were added with stirring 0.8 parts of 'CR-5L' (a hydrophilic epoxy resin manufactured by Dainippon Ink & Chemicals, Inc.) and 24 parts of methyl ethyl ketone, and the glass beads were then removed by filtration.

[0133]

87.2 parts of this dispersed liquid was poured into an aqueous solution consisting of 1.2 parts of dimethylethanolamine and 100 parts of water while stirring by means of a Disper to give a dispersed sample.

[0134]

(2) Acid precipitation step

Water was added to the dispersed sample so as to dilute it by a factor of two, and a 1N aqueous solution of phosphoric acid was added thereto while stirring by means of a Disper until the resin became insoluble and adhered to the pigment. The pH at this stage was 5.

[0135]

(3) Filtration and water-washing step

The pigment to which the resin was adhered was suction-filtered, and then water-washed with ion-exchanged water until the pH of the washing exceeded 6, to give a damp cake.

[0136]

(4) Neutralization and redispersion in aqueous medium step

Water was added to the damp cake until it became fluid, a 10% aqueous solution of dimethylethanolamine was added until the pH of the dispersion became 8.5 to 9.5 while stirring by means of a Disper, and the stirring was then continued for 1 hour in that state. Water was added to the redispersion to adjust the nonvolatile content to 20%.

[0137]

(5) Cross-linking step

The redispersion was subjected to a cross-linking reaction at 95°C for 1 hour, and an aqueous pigment dispersion (B-1) was obtained.

[0138]

(Comparative Example 4)

The procedure of Example 2 was repeated except that the amount of the resin solution B used was 16 parts, no epoxy resin was used, and a 1N aqueous solution of hydrochloric acid was used instead of the 1N aqueous solution of phosphoric acid, and an aqueous pigment dispersion (b-1) was obtained.

[0139]

(Comparative Example 5)

The procedure of Example 2 was repeated except that, after the dispersed sample obtained in the pigment dispersion step of Example 2 was subjected to solvent removal, cross-linking was carried out, and an aqueous pigment dispersion (b-2) was obtained.

[0140]

(Example 3)

The procedure of Example 1 was repeated except that no melamine resin was used, 16 parts (8 parts as solids content) of the resin solution C was used instead of the resin solution A, the amount of diethylethanolamine used was 0.80 parts, a 1N aqueous solution of phosphoric acid was used instead of the 1N aqueous solution of hydrochloric acid so as to carry out acid precipitation until the pH became 5, and a cross-linking reaction was carried out at 95°C for 1 hour without using 'Nacure 2500X', and a self cross-linking type aqueous pigment dispersion (C-1) was obtained.

[0141]

(Example 4)

The procedure of Example 1 was repeated except that no melamine resin was used, 16 parts (8 parts as solids content) of the resin solution D was used instead of the resin solution A, a cross-linking reaction was carried out at 120°C for 1 hour, and a self cross-linking type aqueous pigment dispersion (D-1) was obtained.

[0142]

(Example 5)

The procedure of Example 1 was repeated except that no melamine resin was used, 16 parts (8 parts as solids content) of the resin solution E was used instead of the resin solution A, ammonium persulphate was used at 0.5% of the resin solids content instead of 'Nacure 2500X', and a cross-linking reaction was carried out at 90°C for 3 hours, to give a self cross-linking type aqueous pigment dispersion (E-1).

[0143]

(Example 6)

(1) Pigment dispersion step

A 250 cc glass bottle was charged with 12.8 parts (6.4 parts as solids content) of the resin solution F, 8 parts of 'Fastogen Blue FGF' powder (a copper phthalocyanine pigment manufactured by Dainippon Ink & Chemicals, Inc.), and 40 parts of methyl ethyl ketone together with 130 parts of glass beads having an average diameter of 1.5 mm, and kneading was carried out for 4 hours by means of a paint shaker.

[0144]

To this kneaded material, 2.29 parts (1.6 parts as solids content) of 'Nikarack MX-041', 0.04 parts of 'Nacure 2500X', and 24 parts of methyl ethyl ketone were added with stirring and the glass beads were then removed by filtration.

[0145]

87.13 parts of this dispersed liquid was poured into an aqueous solution consisting of 0.65 parts of dimethylethanolamine and 100 parts of water while stirring by means of a Disper, and the solvent was removed under reduced pressure to give a dispersed sample.

[0146]

(2) Acid precipitation step to cross-linking steps

The procedure of Example 1 was repeated except that a cross-linking reaction was carried out at 95°C for 1 hour in the cross-linking step using this dispersed sample without using 'Nacure 2500X', that is, the acid precipitation step, the filtration and water-washing step, the neutralization and redispersion in aqueous medium step, and the cross-linking step were carried out in that order to give an aqueous pigment dispersion (F-1).

[0147]

(Example 7)

After a cross-linking reaction was carried out at 95°C for 2 hours using the dispersed sample obtained in the pigment dispersion step of Example 6, , the acid precipitation step, the filtration and water-washing step, and the neutralization and redispersion in aqueous medium step were carried out in that order in the same manner as in Example 1, and an aqueous pigment dispersion (F-2) was obtained.

[0148]

(Comparative Example 6)

(1) Pigment dispersion step

A 250 cc glass container was charged with 16 parts (8 parts as solids content) of the resin solution F, 8 parts of 'Fastogen Blue FGF' powder, and 40 parts of methyl ethyl ketone together with 130 parts of glass beads having an average diameter of 1.5 mm, and kneading was carried out for 4 hours by means of a paint shaker.

[0149]

To this kneaded material, 24 parts of methyl ethyl ketone were added with stirring and the glass beads were then removed by filtration.

[0150]

88 parts of this dispersed liquid was poured into an aqueous solution consisting of 0.8 parts of dimethylethanolamine and 100 parts of water while stirring by means of a Disper, and the solvent was removed under reduced pressure to give a dispersed sample.

[0151]

(2) Acid precipitation step to neutralization and redispersion in aqueous medium steps

Using this dispersed sample, the procedure of Example 1 was repeated except that the cross-linking step was not carried out, that is, the acid precipitation step, the filtration and water-washing step, and the neutralization and redispersion in aqueous medium step were carried out in that order to give an aqueous pigment dispersion (f-1).

[0152]

(Comparative Example 7)

The procedure of Example 6 was repeated except that the acid precipitation step was not carried out, to give an aqueous pigment dispersion (f-2).

[0153]

(Example 8)

(1) Pigment dispersion step

After 7.2 parts (3.6 parts as solids content) of the resin solution G was neutralized with 0.31 parts of dimethylethanolamine, it was mixed with 0.4 parts of 'CR-5L', and 43.1 parts of water was added dropwise while stirring to give an aqueous dispersion.

[0154]

To this aqueous dispersion was added 8 parts of 'Symuler Fast Red 4195' (an insoluble azo pigment manufactured by Dainippon Ink & Chemicals, Inc.) and 130 parts of glass beads, kneading was carried out by means of a paint shaker for 4 hours, and the glass beads were then removed by filtration to give a dispersed sample.

[0155]

(2) Acid precipitation step

Water was added to the dispersed sample so as to dilute it by a factor of two, and a 1N aqueous solution of phosphoric acid was added while stirring by means of a Disper until the resin became insoluble and adhered to the pigment. The pH at this stage was 5.

[0156]

(3) Filtration and water-washing step

The pigment to which the resin was adhered was suction-filtered and then water-washed with ion-exchanged water until the pH of the washing exceeded 6 to give a damp cake.

[0157]

(4) Neutralization and redispersion in aqueous medium step

Water was added to the damp cake until it became fluid, 10% aqueous ammonia was added until the pH of the dispersion became 8.5 to 9.5 while stirring by means of a Disper, and the stirring was then continued in that state for 1 hour. Water was added to the redispersion to adjust the nonvolatile content to 20%.

[0158]

(5) Cross-linking step

The redispersion was subjected to a cross-linking reaction at 95°C for 1 hour, and an aqueous pigment dispersion (G-1) having a dispersion resin/pigment ratio of 1/2 as a solids content ratio was obtained.

[0159]

(Comparative Example 8)

As in Example 8, but the pigment was kneaded using 8 parts of the resin solution G (4 parts as solids content) without using 'CR-5L', acid precipitation, filtration and water-washing were subsequently carried out, the mixture was then neutralized with aqueous ammonia so as to disperse it in water, and a noncross-linked aqueous pigment dispersion (g-1) having a dispersion resin/pigment solids content ratio of 1/2 was obtained.

[0160]

(Comparative Example 9)

As in Example 8, but the resin solution G was neutralized with aqueous ammonia, the solvent was removed without carrying out acid precipitation, cross-linking was then carried out, and an aqueous pigment dispersion (g-2) having a dispersion resin/pigment ratio of 1/2 as a solids content ratio was obtained.

[0161]

The constitutions of the various types of aqueous pigment dispersions thus obtained are shown together in Table 1 below.

[0162]

[Table 1]

	Aqueous pigment Dispersion	Resin		Dispersion step		Pigment
		Type	Acid value	Acid precipitation	Cross-linking agent	
Ex. 1	A-1	Acrylic	70	Yes	Melamine	PSK slurry
Comp. Ex. 1	a-1	"	70	-	-	PSK slurry
Comp. Ex. 2	a-2	"	70	Yes	-	PSK slurry
Comp. Ex. 3	a-3	"	70	-	Melamine	PSK slurry
Ex. 2	B-1	"	100	Yes	Epoxy	PSK
Comp. Ex. 4	b-1	"	100	Yes	-	PSK
Comp. Ex. 5	b-2	"	100	-	Epoxy	PSK
Ex. 3	C-1	"	70	Yes	Self cross-linking	PSK slurry
Ex. 4	D-1	"	70	Yes	Self cross-linking	PSK slurry
Ex. 5	E-1	"	67	Yes	Self cross-linking	PSK slurry
Ex. 6	F-1	Polyester	61	Yes	Melamine	FGF
Ex. 7	F-2	"	61	Yes	Melamine	FGF
Comp. Ex. 6	f-1	"	61	Yes	-	FGF
Comp. Ex. 7	f-2	"	61	-	Melamine	FGF
Ex. 8	G-1	Polyurethane	54	Yes	Epoxy	4195
Comp. Ex. 8	g-1	"	54	Yes	-	4195
Comp. Ex. 9	g-2	"	54	-	Epoxy	4195

[0163]

In the table above, PSK denotes 'Fastogen Super Maroon PSK', FGF denotes 'Fastogen Blue FGF', and 4195 denotes 'Symuler Fast Red 4195'.

[0164]

(Example 9)

'Watersol S-751' (a water-soluble acrylic resin for stoving paint having a nonvolatile content of 50%, manufactured by Dainippon Ink & Chemicals, Inc.) 56 parts (28 parts as solids content)

'Cymel 303' (a methoxylated melamine resin having 98% effective component, manufactured by Mitsui Cyanamid) 12.25 parts (12 parts as solids content) and

aqueous pigment dispersion (A-1) 100 parts (20 parts as solids content) were mixed at the above-mentioned ratio, water was added so as to dilute to a nonvolatile content of 24%, and a water-soluble acrylic resin stoving paint was prepared.

[0165]

This paint was applied using a bar coater on 'BT-144 treated steel sheet' (a zinc phosphate treated steel sheet manufactured by Nihon Parkerizing Co., Ltd.) at a film thickness of $20 \pm 2 \mu\text{m}$, and after setting for 10 minutes was stoved at 150°C for 20 minutes to give a test piece.

[0166]

This paint was also applied using a bar coater to a corona discharge-treated PET film at a film thickness of $10 \pm 1 \mu\text{m}$, and after setting for 10 minutes was stoved at 150°C for 20 minutes to give a test piece.

[0167]

(Comparative Examples 10 to 12)

The procedure of Example 9 was repeated except that the aqueous pigment dispersions (a-1), (a-2) and (a-3) were used instead of the aqueous pigment dispersion (A-1) to prepare water-soluble acrylic resin stoving paints, and test pieces were made.

[0168]

(Example 10)

The procedure of Example 9 was repeated except that the aqueous pigment dispersion (B-1) was used instead of the aqueous pigment dispersion (A-1) to prepare a water-soluble acrylic resin stoving paint, and a test piece was made.

[0169]

(Comparative Examples 13 and 14)

The procedure of Example 9 was repeated except that aqueous pigment dispersions (b-1) and (b-2) were used instead of the aqueous pigment dispersion (A-1) to prepare water-soluble acrylic resin stoving paints, and test pieces were made.

[0170]

(Examples 11 to 13)

The procedure of Example 9 was repeated except that the aqueous pigment dispersions (C-1), (D-1) and (E-1) were used instead of the aqueous pigment dispersion (A-1) to prepare water-soluble acrylic resin stoving paints, and test pieces were made.

[0171]

(Examples 14 and 15)

The procedure of Example 9 was repeated except that 43 parts (28 parts as solids content) of 'Watersol S-212' (a water-soluble polyester resin for stoving paint having a nonvolatile content of 65% manufactured by Dainippon Ink & Chemicals, Inc.) was used instead of the 'Watersol S-751', the aqueous pigment dispersions (F-1) and (F-2) were used instead of the aqueous pigment dispersion (A-1) to prepare water-soluble polyester resin stoving paints, and test pieces were made.

[0172]

(Comparative Examples 15 and 16)

The procedure of Example 14 was repeated except that the aqueous pigment dispersions (f-1) and (f-2) were used instead of the aqueous pigment dispersion (F-1) to prepare water-soluble polyester resin stoving paints, and test pieces were made.

[0173]

(Example 16)

'Hydran AP-40' and an aqueous pigment dispersion were mixed in the solids content weights below:

'Hydran AP-40' (a water-soluble polyurethane resin having a nonvolatile content of 22.5%, manufactured by Dainippon Ink & Chemicals, Inc.) 178 parts (40 parts as solids content)

Aqueous pigment dispersion (G-1) 300 parts (60 parts as solids content), and 10 parts of ethanol was added to prepare a water-based ink having a nonvolatile content of 20%.

[0174]

This ink was applied was applied to a corona discharge-treated PET film using a No. 7 bar coater, then dried at 60°C for 1 minute to give a sample.

[0175]

(Comparative Example 17 and 18)

The procedure of Example 16 was repeated except that the aqueous pigment dispersions (g-1) and (g-2) were used instead of the aqueous pigment dispersion (G-1) to prepare water-based inks, and samples were made.

[0176]

(Example 17)

First, a printing paste was prepared as follows.

50 parts of 'Ryudai W Reducer Conc 500' (a viscosity increasing agent manufactured by Dainippon Ink & Chemicals, Inc.), 650 parts of mineral spirit, and 300 parts of water were weighed in a beaker, and they were stirred with a Homomixer for 30 minutes.

[0177]

Next, a printing agent was prepared by mixing as follows.

1.0 parts (0.1 parts as pigment content) of the aqueous pigment dispersion (A-1), 1.0 part of water, 16.0 parts of the above-mentioned printing paste, and 2.0 parts of 'Ryudai W Fixer 756K-1' (an acrylic resin emulsion manufactured by Dainippon Ink & Chemicals, Inc.) were weighed in a beaker, and they were stirred with a Homomixer for 30 minutes to give a printing agent.

[0178]

A printing agent as a standard sample was prepared as follows.

Preparation of colour base

15.0 parts of 'Fastogen Super Maroon PSK', 7.2 parts of 'Emulgen 911' (a surfactant manufactured by Kao Corporation), and 77.8 parts of water were weighed in a 250 cc glass bottle together with 130 g of glass beads having an average diameter of 1.5 mm, and kneading was carried out using a paint shaker for 4 hours to give a colour base.

[0179]

Next, 0.67 parts (0.1 parts as pigment content) of the above-mentioned colour base, 1.33 parts of water, 16.00 parts of the printing paste, and 2.00 parts of 'Ryudai W Fixer 756K-1' were weighed in a beaker and stirred with a Homomixer for 30 minutes to give a standard printing agent.

[0180]

The printing agent thus prepared was applied using a doctor to a cotton satin using a 90 mesh screen, and dried at 120°C for 5 minutes to give a test cloth.

[0181]

(Comparative Examples 19 to 21)

The procedure of Example 17 was repeated except that the aqueous pigment dispersions (a-1), (a-2), and (a-3) were used instead of the aqueous pigment dispersion (A-1) to prepare printing agents, and test cloths were prepared.

[0182]

(Example 18)

The procedure of Example 17 was repeated except that the aqueous pigment dispersion (B-1) was used instead of the aqueous pigment dispersion (A-1) to prepare a printing agent, and a test cloth was prepared.

[0183]

(Comparative Examples 22 and 23)

The procedure of Example 17 was repeated except that the aqueous pigment dispersions (b-1) and (b-2) were used instead of the aqueous pigment dispersion (A-1) to prepare printing agents, and test cloths were prepared.

[0184]

<Evaluation>

(1) Volume average particle size

The volume average particle size was measured using a 'UPA-150' (Laser-Doppler type particle size distribution analyser manufactured by Nikkiso Co., Ltd.) for samples immediately after the aqueous pigment dispersions were prepared in the Examples and Comparative Examples, and for samples that had been allowed to stand at room temperature for 30 days. The results are given in Table 2.

[0185]

[Table 2]

	Resin		Pigment	Aqueous pigment Dispersion	Particle size (nm)	
	Type	Acid value			Immediately after	30 days after
Ex. 1	Acrylic	70	PSK slurry	A-1	155	155
Comp. Ex. 1	"	70	PSK slurry	a-1	215	300
Comp. Ex. 2	"	70	PSK slurry	a-2	160	165
Comp. Ex. 3	"	70	PSK slurry	a-3	220	230
Ex. 2	"	100	PSK	B-1	160	160
Comp. Ex. 4	"	100	PSK	b-1	160	165
Comp. Ex. 5	"	100	PSK	b-2	265	280
Ex. 3	"	70	PSK slurry	C-1	150	155
Ex. 4	"	70	PSK slurry	D-1	170	170
Ex. 5	"	67	PSK slurry	E-1	155	160
Ex. 6	Polyester	61	FGF	F-1	145	145
Ex. 7	"	61	FGF	F-2	145	150
Comp. Ex. 6	"	61	FGF	f-1	140	145
Comp. Ex. 7	"	61	FGF	f-2	205	210
Ex. 8	Polyurethane	54	4195	G-1	185	190
Comp. Ex. 8	"	54	4195	g-1	180	180
Comp. Ex. 9	"	54	4195	g-2	240	245

[0186]

From the results shown in Table 2 it can be seen that the aqueous pigment dispersions obtained by the production process of the present invention have substantially constant particle sizes during the period from immediately after production until 30 days after production, and the dispersion stability is excellent. On the other hand, since the aqueous pigment dispersions obtained in Comparative Examples 1, 3, 5, 7, and 9 had not been subjected to acid precipitation, their dispersion stability was poor. Although the aqueous pigment dispersions obtained in Comparative Examples 2, 6, and 8 gave excellent dispersion stability due to the acid precipitation, since they had not been cross-linked using a cross-linking agent, as hereinafter described, the water resistance of the coating was poor.

[0187]

(2) Evaluation as stoving paint

The paints obtained in Examples 9 to 15 and Comparative Examples 10 to 16 were evaluated as follows. The results for the water-soluble acrylic resin stoving paints are given in Table 3, and the results for the water-soluble polyester resin stoving paints are given in Table 4.

[0188]

Gloss: A 'BT-144 treated steel sheet' was coated and the 60° specular gloss was measured.

[0189]

Colouring properties: A PET film was coated and evaluated visually.

Evaluation criteria

A: High colour density and hiding power.

[0190]

B: Colour density and hiding power a little inferior.

C: Quite poor colour density and hiding power.

D: Quite poor colour density and hiding power, and low sharpness.

[0191]

Water resistance: A 'BT-144 treated steel sheet' was coated, it was immersed in water at 50°C, and the occurrence of blisters was assessed visually after 96 hours.

Evaluation criteria

A: No abnormalities.

[0192]

B: Slight blistering noticeable.

C: Quite a lot of blistering noticeable.

D: Blistering over the entire surface of the test piece.

[0193]

[Table 3]

	Aqueous pigment dispersion	Dispersed resin acid value	60° Gloss	Colouring Properties	Water Resistance
Ex. 9	A-1 (acid precipitation, cross-linking)	70	93	A	A
Comp. Ex. 10	a-1	70	88	C	C
Comp. Ex. 11	a-2 (acid precipitation)	70	94	B-A	C
Comp. Ex. 12	a-3 (cross-linking)	70	79	D-C	A
Ex. 10	B-1 (acid precipitation, cross-linking)	100	94	A	B-A
Comp. Ex. 13	b-1 (acid precipitation)	100	94	A	D
Comp. Ex. 14	b-2 (cross-linking)	100	71	C	B-A
Ex. 11	C-1 (acid precipitation, self cross-linking)	70	94	A	A
Ex. 12	D-1 (acid precipitation, self cross-linking)	70	92	B-A	A
Ex. 13	E-1 (acid precipitation, self cross-linking)	67	93	B-A	A

[0194]

[Table 4]

	Aqueous pigment dispersion	Dispersed resin acid value	60° Gloss	Colouring Properties	Water Resistance
Ex. 14	F-1 (acid precipitation, cross-linking)	61	94	A	B-A
Ex. 15	F-2 (acid precipitation, cross-linking)	61	93	B-A	B-A
Comp. Ex. 15	f-1 (acid precipitation)	61	96	A	C
Comp. Ex. 16	f-2 (cross-linking)	61	81	C	B-A

[0195]

From the results shown in Table 3 and Table 4 it can be seen that the paints employing the aqueous pigment dispersions obtained by the production process of the present invention have excellent gloss, colouring properties, and water resistance.

[0196]

(3) Evaluation as water-based ink

The water-based inks obtained in Example 16 and Comparative Examples 17 to 18 were evaluated as follows. The results are given in Table 5.

[0197]

Gloss: 60° specular gloss.

Colouring properties: the same evaluation as for the stoving paints

Water resistance : A rubbing tester manufactured by Oohira Rika Kogyo K.K. was used, and rubbing was carried out 10 times by means of water-soaked felt with a load of 0.1 kg.

[0198]

Evaluation criteria

A: No colour was transferred to the felt.

B: The felt was slightly coloured.

[0199]

C: The felt was considerably coloured, and the ink partially peeled off the test piece.

D: The felt was intensely coloured, and the ink peeled off the test piece.

[0200]

[Table 5]

	Aqueous pigment dispersion	Dispersed resin acid value	60° Gloss	Colouring Properties	Water Resistance
Ex. 16	G-1 (acid precipitation, cross-linking)	54	80	A	B-A
Comp. Ex. 17	g-1 (acid precipitation)	54	81	B-A	D-C
Comp. Ex. 18	g-2 (cross-linking)	54	71	D-C	B

[0201]

From the results shown in Table 5 it can be seen that the water-based inks employing the aqueous pigment dispersions obtained by the production process of the present invention have excellent gloss and colouring properties.

[0202]

(4) Evaluation as printing agent

The printing agents obtained in Examples 17 to 18 and Comparative Examples 19 to 23 were evaluated as follows. The results are given in Table 6.

Colouring power: the colouring power was measured using a spectrophotometer, and the colouring powers of the Examples and Comparative Examples were expressed as a % relative to a 100% test cloth coated with a dispersion of the standard printing agent dispersed using an emulsifier.

Water resistance: A rubbing tester manufactured by Oohira Rika Kogyo K.K. was used, and rubbing was carried out 50 times by means of water-soaked felt with a load of 1 kg.

[0203]

Evaluation criteria

A: No colour was transferred to the felt.

B: The felt was slightly coloured.

[0204]

C: The felt was considerably coloured, and fading of the colour of the test piece was observed.

D: The felt was intensely coloured, and the colour of the test piece faded considerably.

[0205]

[Table 6]

	Aqueous pigment dispersion	Dispersed resin acid value	Colouring power (%)	Water Resistance
Ex. 17	A-1 (acid precipitation, cross-linking)	70	151	A
Comp. Ex. 19	a-1	70	96	C-B
Comp. Ex. 20	a-2 (acid precipitation)	70	155	C-B
Comp. Ex. 21	a-3 (cross-linking)	70	100	A
Ex. 18	B-1 (acid precipitation, cross-linking)	100	156	B-A
Comp. Ex. 22	b-1 (acid precipitation)	100	150	D-C
Comp. Ex. 23	b-2 (cross-linking)	100	92	B-A

[0206]

From the results shown in Table 6 it can be seen that the printing agents employing the aqueous pigment dispersions obtained by the production process of the present invention have excellent colouring power and water resistance.

[0207]

[Effects of the Invention]

By virtue of acid precipitation, the aqueous pigment dispersion obtained in accordance with the production process of the present invention has excellent storage stability, and when it is used in a water-based paint, a water-based ink, and a printing agent, it gives excellent gloss, colouring properties and colouring power. Furthermore, by virtue of cross-linking, it gives excellent water resistance, and it is extremely useful.